SUMMARY PROBLEM

(a) (1) $HNic(aq) \rightleftharpoons H^+(aq) + Nic^-(aq)$ $K_a = 1.4 \times 10^{-5}$

$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O$ $\frac{1}{K_W} = \frac{1}{1.0 \times 10^{-14}}$

$HNic(aq) + OH^-(aq) \rightleftharpoons Nic^-(aq) + H_2O$ $K = 1.4 \times 10^{-9}$

(2) $Nic^-(aq) + H^+(aq) \rightleftharpoons HNic(aq)$ $K = \frac{1}{K_a} = \frac{1}{1.4 \times 10^{-5}} = 7.1 \times 10^4$

(3) $HNic(aq) \rightleftharpoons H^+(aq) + Nic^-(aq)$ $K_a = 1.4 \times 10^{-5}$

$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq)$ $\frac{1}{K_a} = \frac{1}{6.9 \times 10^{-4}}$

$HNic(aq) + F^-(aq) \rightleftharpoons HF(aq) + Nic^-(aq)$ $K = 0.020$

(b) (1) mol HNic = 0.295 mol/L × (1.25 L) = 0.369 mol Nic^- = $47.13\text{ g} \times \frac{1\text{ mol}}{145.1\text{ g}} = 0.325$

$[H^+] = 1.4 \times 10^{-5} \times \frac{0.369}{0.325} = 1.6 \times 10^{-5}$; pH = 4.80

(2) H^+ reacts with Nic^- to produce more HNic; Nic^- is used up.

$[H^+] = 1.4 \times 10^{-5} \times \frac{0.369 + 0.100}{0.325 - 0.100} = 2.9 \times 10^{-5}$; pH = 4.53

(3) mol OH^- = $5.00\text{ g} \times \frac{1\text{ mol}}{40.0\text{ g}} = 0.125$

OH^- reacts with HNic to produce more Nic^-; HNic is used up.

$[H^+] = 1.4 \times 10^{-5} \times \frac{0.369 - 0.125}{0.325 + 0.125} = 7.6 \times 10^{-6}$; pH = 5.11

(4) mol H^+ = 0.095 L × (5.00 mol/L) = 0.475

H^+ reacts with Nic^-; Nic^- is limiting, so it is consumed.

H^+ left over from reaction = 0.475 − 0.325 = 0.150; H^+ contribution of HNic is negligible.

$[H^+] = \frac{0.150\text{ mol}}{0.095\text{ L} + 1.25\text{ L}} = 0.112\ M$; pH = 0.95

(5) Let x = the number of moles of HNic used by reacting with OH^- = number of moles of Nic^-

$[H^+] = 10^{-5.50} = 3.16 \times 10^{-6}$

$3.16 \times 10^{-6} = 1.4 \times 10^{-5} \times \frac{0.369 - x}{0.325 + x}$ $x = 0.24$

0.24 mol HNic must react with 0.24 mol OH^-.

mass NaOH = 0.24 mol × (40.0 g/mol) = 9.6 g

(c) (1) $1.4 \times 10^{-5} = \dfrac{[H^+]^2}{0.575 - [H^+]}$. Assume $[H^+] << 0.575$; $[H^+] = 2.8 \times 10^{-3}$

% ionization = $\dfrac{2.8 \times 10^{-3}}{0.575} \times 100 < 5\%$; so the assumption is valid. pH = 2.55

(2) mol HNic = 0.040 L × 0.575 mol/L = 0.0230 = moles OH^- required

0.023 mol OH^- = 0.0230 mol KOH × $\dfrac{1\text{ L}}{0.335\text{ mol}}$ = 0.0687 L = 68.7 mL

(3) At half neutralization; $[H^+] = K_a = 1.4 \times 10^{-5}$; pH = 4.85

(4) At equivalence point: V = (0.0687 + 0.0400) L = 0.1087 L

mol Nic^- = mol HNic = 0.0230; $[Nic^-] = \dfrac{0.0230\text{ mol}}{0.1087\text{ L}} = 0.216\ M$

$7.1 \times 10^{-10} = \dfrac{[OH^-]^2}{0.216 - [OH^-]}$; assume $[OH^-] << 0.216$ $[OH^-] = 1.2 \times 10^{-5}$

% ionization << 5% ; pOH = 4.91; pH = 9.08

PROBLEMS

1. (a) $NH_3(aq) + HF(aq) \rightleftharpoons NH_4^+(aq) + F^-(aq)$ (b) $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O$

   (c) $SO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HSO_3^-(aq)$ (d) $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O$

3. (a) $F^-(aq) + H^+(aq) \rightleftharpoons HF(aq)$ (b) $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O$

   (c) $H_2PO_4^-(aq) + H^+(aq) \rightleftharpoons H_3PO_4(aq)$

5. (a) $NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$ $1/K_a = 1/(5.6 \times 10^{-10})$

   $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$ $K_a = 6.9 \times 10^{-4}$

   $NH_3(aq) + HF(aq) \rightleftharpoons NH_4^+(aq) + F^-(aq)$ $K = 1.2 \times 10^6$

   (b) $K = 1/K_W = 1.0 \times 10^{14}$

   (c) $K = 1/K_a\ HSO_3^- = 1/(6.0 \times 10^{-8}) = 1.7 \times 10^7$

   (d) $K = 1/K_W = 1.0 \times 10^{14}$

7. (a) $K = 1/K_a\ HF = 1/(6.9 \times 10^{-4}) = 1.4 \times 10^3$

   (b) $K = 1/K_W = 1.0 \times 10^{14}$

   (c) $K = 1/K_a\ H_3PO_4 = 1/(7.1 \times 10^{-3}) = 1.4 \times 10^2$

9. $[H^+] = K_a \times \frac{[HLac]}{[Lac^-]}$; $[H^+] = 1.4 \times 10^{-4} \times \frac{[HLac]}{[Lac^-]}$

(a) $[H^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.250}$; $[H^+] = 1.4 \times 10^{-4}$; pH = 3.85

(b) $[H^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.125}$; $[H^+] = 2.8 \times 10^{-4}$; pH = 3.55

(c) $[H^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.0800}$; $[H^+] = 4.4 \times 10^{-4}$; pH = 3.36

(d) $[H^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.0500}$; $[H^+] = 7.0 \times 10^{-4}$; pH = 3.15

11. $[H^+] = K_a \times \frac{n_{HA}}{n_{A^-}}$; $[H^+] = K_a \times \frac{\text{mol } HNO_2}{\text{mol } NO_2^-}$; $[H^+] = 6.0 \times 10^{-4} \times \frac{(0.2500 \text{ L})(0.0410 \text{ mol/L})}{0.0250 \text{ mol}}$

$[H^+] = 2.5 \times 10^{-4}$; pH = 3.61

13. (a) mol $HC_2H_3O_2 = \frac{12.50 \text{ g}}{60.1 \text{ g/mol}} = 0.208$; mol $C_2H_3O_2^- = \frac{15.00 \text{ g}}{82.0 \text{ g/mol}} = 0.183$

$[H^+] = 1.8 \times 10^{-5} \times \frac{0.208}{0.183} = 2.0 \times 10^{-5}$; pH = 4.70

(b) pH = 4.70

15. Find K_b: pH = 8.73 ; $[H^+] = 1.9 \times 10^{-9}\ M$; $[OH^-] = (1.0 \times 10^{-14})/(1.9 \times 10^{-9}) = 5.3 \times 10^{-6}\ M$

$[X^-] = [NaX] = 0.614 \text{ mol}/2.50 \text{ L} = 0.246\ M$

$K_b = \frac{[OH^-]^2}{[X^-]} = \frac{(5.3 \times 10^{-6})^2}{0.246} = 1.14 \times 10^{-10}$

Find K_a: $K_a = (1.0 \times 10^{-14})/(1.14 \times 10^{-10}) = 8.8 \times 10^{-5}$

$[H^+] = K_a \times \frac{\text{mol HX}}{\text{mol } X^-} = 8.8 \times 10^{-5} \times \frac{0.219}{0.614} = 3.1 \times 10^{-5}$; pH = 4.50

17. mol SnF_2 = (0.250 L)(0.150 mol/L) = 0.0375 ; mol F^- = 2(mol SnF_2) = 0.0750

(a) 0.0750 mol F^- + 0.100 mol H^+ ; no buffer; all the F^- is used up

(b) 0.060 mol H^+ produces 0.060 mol HF and uses up 0.0150 mol F^-

Resulting solution: 0.060 mol HF + 0.0150 mol F^-

Solution is a buffer.

(c) 0.040 mol H^+ produces 0.040 mol HF and uses up 0.040 mol F^-.

Resulting solution: 0.040 mol HF + 0.0350 mol F^-.

Solution is a buffer.

(d) No. The resulting solution has a strong base, NaOH and a weak base F^-.

(e) Yes. The resulting solution has 0.040 mol HF and 0.0750 mol F^-.

19. mol HOBr = (2.50 g)(1 mol/96.9 g) = 0.0258

mol OH^- = mol KOH = (0.750 g)(1 mol/56.1 g) = 0.0134

The reaction between HOBr and KOH produces 0.0134 mol OBr^- and leaves 0.0124 mol HOBr.

$[H^+] = 2.5 \times 10^{-9} \times \dfrac{0.0124}{0.0134} = 2.3 \times 10^{-9}$; pH = 8.64

21. mol $HC_4H_7O_2$ = (2.00 g)(1 mol/88.1 g) = 0.0227

mol OH^- = mol NaOH = (0.50 g)(1 mol/40.0 g) = 0.0125

The reaction between $HC_4H_7O_2$ and OH^- produces 0.0125 mol $C_4H_7O_2^-$.

mol $HC_4H_7O_2$ unreacted = 0.0227 − 0.0125 = 0.0102

$[H^+] = 1.5 \times 10^{-5} \times \dfrac{0.0102}{0.0125} = 1.2 \times 10^{-5}$; pH = 4.91

23. (a) $HF - F^-$ (b) $H_2CO_3 - HCO_3^-$ (c) $HPO_4^{2-} - PO_4^{3-}$

25. pH = 9.40 ; $[H^+] = 4.0 \times 10^{-10}\ M$

(a) $4.0 \times 10^{-10} = 4.7 \times 10^{-11} \times \dfrac{[HCO_3^-]}{[CO_3^{2-}]}$; ratio = $\dfrac{4.0 \times 10^{-10}}{4.7 \times 10^{-11}} = 8.5$

(b) mol CO_3^{2-} = mol Na_2CO_3 = (1.00 L)(0.225 mol/L) = 0.225

$\dfrac{[HCO_3^-]}{[CO_3^{2-}]} = \dfrac{\text{mol } HCO_3^-}{\text{mol } CO_3^{2-}}$; $8.5 = \dfrac{\text{mol } HCO_3^-}{0.225}$; mol HCO_3^- = 1.9

(c) mol HCO_3^- = (0.475 L)(0.336 mol/L) = 0.160

$8.5 = \dfrac{0.160}{\text{mol } CO_3^{2-}}$; mol CO_3^{2-} = 0.0188 ; mol Na_2CO_3 = mol CO_3^{2-}

mass Na_2CO_3 = (0.0188 mol)(106 g/mol) = 2.0 g

(d) mol CO_3^{2-} = mol Na_2CO_3 = (0.735 L)(0.139 mol/L) = 0.102

$8.5 = \frac{\text{mol } HCO_3^-}{0.102}$; mol HCO_3^- = 0.86 ; mol Na_2CO_3 = mol CO_3^{2-}

$V = 0.86 \text{ mol} \times \frac{1 \text{ L}}{0.200 \text{ mol}} = 4.3 \text{ L}$

27.	Base	Acid
(a)	0.250 M	0.250 M
(b)	0.250 M	0.125 M
(c)	0.250 M	0.0800 M
(d)	0.250 M	0.0500 M

29. mol $H_2PO_4^-$ = mol KH_2PO_4 = (0.300 L)(0.500 mol/L) = 0.150

mol HPO_4^{2-} = mol K_2HPO_4 = (0.300 L)(0.317 mol/L) = 0.0951

(a) $[H^+] = 6.2 \times 10^{-8} \times \frac{\text{mol } H_2PO_4^-}{\text{mol } HPO_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.150}{0.0951} = 9.8 \times 10^{-8}$; pH = 7.01

(b) HCl (H^+) reacts with HPO_4^{2-} to use up 0.0500 mol HPO_4^{2-} and make 0.0500 mol $H_2PO_4^-$.

mol $H_2PO_4^-$ = 0.150 + 0.0500 = 0.200 ; mol HPO_4^{2-} = 0.0951 − 0.0500 = 0.0451

$[H^+] = 6.2 \times 10^{-8} \times \frac{\text{mol } H_2PO_4^-}{\text{mol } HPO_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.200}{0.0451} = 2.7 \times 10^{-7}$; pH = 6.56

(c) NaOH (OH^-) reacts with $H_2PO_4^-$ to use up 0.0500 mol $H_2PO_4^-$ and make 0.0500 mol HPO_4^{2-}.

mol $H_2PO_4^-$ = 0.150 − 0.0500 = 0.100 ; mol HPO_4^{2-} = 0.0951 + 0.0500 = 0.1451

$[H^+] = 6.2 \times 10^{-8} \times \frac{\text{mol } H_2PO_4^-}{\text{mol } HPO_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.100}{0.1451} = 4.3 \times 10^{-8}$; pH = 7.37

31. (a) mol $H_2PO_4^-$ = mol KH_2PO_4 = (10.0 L)(0.500 mol/L) = 5.00

mol HPO_4^{2-} = mol K_2HPO_4 = (10.0 L)(0.317 mol/L) = 3.17

$[H^+] = 6.2 \times 10^{-8} \times \frac{\text{mol } H_2PO_4^-}{\text{mol } HPO_4^{2-}} = 6.2 \times 10^{-8} \times \frac{5.00}{3.17} = 9.8 \times 10^{-8}$; pH = 7.01

(b) Before dilution (from Problem 29):

mol $H_2PO_4^-$ = mol KH_2PO_4 = (0.300 L)(0.500 mol/L) = 0.150

mol HPO_4^{2-} = mol K_2HPO_4 = (0.300 L)(0.317 mol/L) = 0.0951

After dilution to 10.0 L, and taking 0.600 L of the buffer:

mol $H_2PO_4^- = \dfrac{0.150 \text{ mol}}{10.0 \text{ L}} \times 0.600 \text{ L} = 0.00900$ mol

mol $HPO_4^{2-} = \dfrac{0.0951 \text{ mol}}{10.0 \text{ L}} \times 0.600 \text{ L} = 0.005571$ mol

H^+ added = 0.0500 mol; HPO_4^{2-} is limiting and used up. Mol H^+ left = 0.0500 − 0.00571 = 0.0443

$[H^+]$ = 0.0443 mol/0.600 L = 0.0738 M ;   pH = 1.13

(c) as in (b): mol $H_2PO_4^-$ = 0.00900 ;   mol HPO_4^{2-} = 0.00571

mol OH^- added = 0.0500 ; $H_2PO_4^-$ is limiting and used up.

mol OH^- left = 0.0500 − 0.0090 = 0.0410

$[OH^-]$ = 0.0410 mol/0.600 L = 0.0683 M ;   pOH = 1.17 ;   pH = 12.83

(d) (a) is the same; (b) and (c) vary.

(e) Dilution does not change the pH of a buffer but reduces buffer capacity.

33. (a) $[H^+] = K_a \, H_2PO_4^- \times \dfrac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 6.2 \times 10^{-8} \times 3.0 = 1.86 \times 10^{-7}$;   pH = 6.73

(b) ratio of acid to base is 3:1. Using up 15% of base (HPO_4^{2-}) means:

mol HPO_4^{2-} = 1 − (0.15 × 1) = 0.85 ;   mol $H_2PO_4^-$ = 3 + (0.15 × 1) = 3.15

$[H^+] = 6.2 \times 10^{-8} \times \dfrac{3.15}{0.85} = 2.30 \times 10^{-7}\ M$;   pH = 6.64

(c) $[H^+] = 1.0 \times 10^{-7}\ M$; $1.0 \times 10^{-7} = 6.2 \times 10^{-8} \times \dfrac{[H_2PO_4^-]}{[HPO_4^{2-}]}$; $\dfrac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 1.6$

35. pH = 7.40 ; $[H^+] = 4.0 \times 10^{-8}$

(a) $\dfrac{[H_2CO_3]}{[HCO_3^-]} = \dfrac{[H^+]}{K_a \, H_2CO_3} = \dfrac{4.0 \times 10^{-8}}{4.4 \times 10^{-7}} = 0.091$

(b) $\frac{[H_2CO_3]}{[HCO_3^-]} = \frac{0.091}{1}$; Assume $[HCO_3^-] = 1.000\ M$, then $[H_2CO_3] = 0.091\ M$

$[HCO_3^-]$ after conversion to $H_2CO_3 = 1.000 - (0.15 \times 1.000) = 0.85\ M$

$[H_2CO_3]$ after conversion $= 0.091 + (0.15 \times 1.000) = 0.241\ M$

$[H^+] = 4.4 \times 10^{-7}\frac{0.241}{0.85} = 1.25 \times 10^{-7}$; pH = 6.90

(c) From (a) assume $[HCO_3^-] = 1.000\ M$, then $[H_2CO_3] = 0.091\ M$

$[H_2CO_3]$ after conversion $= 0.091 - (0.15 \times 0.091) = 0.077\ M$

$[HCO_3^-]$ after conversion $= 1.000 + (0.15 \times 0.091) = 1.014\ M$

$[H^+] = 4.4 \times 10^{-7} \times \frac{0.077}{1.014} = 3.34 \times 10^{-8}\ M$; pH = 7.48

37. (a) MO (b) PP (c) any (d) MO

39. (a) $pK_a = 8.2$; $K_a = 6.3 \times 10^{-9}$ (b) 7.2 – 9.2 (c) purple

41. (a) mol OH^- = 2(mol $Sr(OH)_2$) = 2[(0.0584 L)(0.218 mol/L)] = 0.0255

mol H^+ = mol HNO_3 = mol OH^- = 0.0255

$[H^+] = [HNO_3] = 0.0255$ mol/0.02500 L = 1.02 M ; pH = 8.6×10^{-3}

(b) 7.00

(c) mol NO_3^- = mol HNO_3 = 0.0255 ; $[NO_3^-] = \frac{0.0255\ \text{mol}}{(0.02500 + 0.0584)\ \text{L}} = 0.305\ M$

mol $Sr^{2+} = \frac{1}{2}$(mol OH^-) $= \frac{0.0255}{2}$; $[OH^-] = \frac{(0.0255/2)\ \text{mol}}{(0.02500 + 0.0584)\ \text{L}} = 0.153\ M$

43. (a) mol NH_4^+ = mol NH_4Cl = (25.00 g)(1 mol/53.49 g) = 0.467

mol OH^- = mol KOH = mol NH_4^+ = 0.467 ; V_{KOH} = (0.467 mol)(1 L/0.114 mol) = 4.10 L

(b) $[Cl^-] = [K^+] = [NH_3] = \frac{0.467\ \text{mol}}{4.10\ \text{L} + 0.178\ \text{L}} = 0.109\ M$

At equivalence: $NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$K_b = \frac{[OH^-]^2}{[NH_3] - [OH^-]}$; assume $[OH^-] \ll [NH_3]$

$1.8 \times 10^{-5} = \frac{[OH^-]^2}{0.109}$; $[OH^-] = 1.40 \times 10^{-3}$; % ionization = 1.28 ; assumption valid

(c) pOH = 2.85 ; pH = 11.15

45. (a) $(CH_3CH_2)_3N\,(aq) + H^+(aq) \rightleftharpoons (CH_3CH_2)_3NH^+(aq)$

(b) mol H^+ = mol $(CH_3CH_2)_3N$ = (0.0200 L)(0.220 mol/L = 0.00440

mol HCl = mol H^+ = 0.00440 ; V_{HCl} = (0.00440 mol)(1L/0.544 mol) = 0.00809 L

(c) mol Cl^- = mol H^+ = mol $(CH_3CH_2)_3NH^+$ = 0.00440

$$[Cl^-] = [(CH_3CH_2)_3NH^+] = \frac{0.00440\text{ mol}}{(0.00809 + 0.0200)\text{ L}} = 0.157\ M$$

$$K_a\ (CH_3CH_2)_3NH^+ = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{5.2 \times 10^{-4}} = 1.9 \times 10^{-11}$$

$[H^+] = [(CH_3CH_2)_3N]$; assume $[H^+] << [(CH_3CH_2)_3NH^+]$

$1.9 \times 10^{-11} = \frac{[H^+]^2}{0.157}$; $[H^+] = 1.7 \times 10^{-6}$; % ionization = 0.0011 ; assumption valid

$[H^+] = [(CH_3CH_2)_3N] = 1.7 \times 10^{-6}\ M$

(d) pH = 5.77

47. (a) $H^+(aq) + OH^-(aq) \rightarrow H_2O$

(b) Ba^{2+}, NO_3^-

(c) mol OH^- = 2(mol $Ba(OH)_2$) = 2[(0.0500 L)(0.237 mol/L)] = 0.0237

mol OH^- = mol H^+ = mol HNO_3 = 0.0237 ; V_{HNO_3} = (0.0237 mol)(1 L/0.4000 mol) = 0.0592 L

(d) $[OH^-] = 2[Ba(OH)_2]$ = 2(0.237) = 0.474 M ; pOH = 0.324 ; pH = 13.68

(e) mol OH^- (half-way) = $\frac{1}{2}$(0.0237) = 0.01185

V_{tot} (half-way) = $(0.05000)_{\text{from } OH^-} + \frac{1}{2}(0.0592)_{\text{from } H^+}$ = 0.0796 L

$[OH^-]$ (half-way) = 0.01185 mol/0.0796 L = 0.149 ; pOH = 0.827 ; pH = 13.17

49. (a) $HBut\,(aq) + OH^-(aq) \rightarrow But^-(aq)$

(b) But^-, Na^+

(c) mol OH^- = mol HBut = (0.0500 L)(0.350 mol/L)] = 0.0175

mol NaOH = mol OH^- = 0.0175 ; V_{NaOH} = (0.0175 mol)(1 L/0.225 mol) = 0.0778 L

(d) $K_a = \frac{[H^+][But^-]}{[HBut] - [H^+]}$; $[H^+] = [But^-]$; assume $[H^+] << [HBut]$

$1.5 \times 10^{-5} = \frac{[H^+]^2}{0.350}$; $[H^+] = 2.29 \times 10^{-3}$; % ionization = 0.65 ; assumption valid ; pH = 2.64

(e) At half-equivalence: $[H^+] = K_a = 1.5 \times 10^{-5}$; pH = 4.82

(f) At the equivalence point: Solution has 0.0175 mol But^- and a volume of (0.0778 + 0.0500) L.

$[But^-] = 0.0175 \text{ mol}/0.1278 \text{ L} = 0.137\ M$; $K_b = \dfrac{1.0 \times 10^{-14}}{1.5 \times 10^{-5}} = 6.7 \times 10^{-10}$

$K_b = \dfrac{[HBut][OH^-]}{[But^-] - [OH^-]}$; $[HBut] = [OH^-]$; assume $[OH^-] \ll [But^-]$

$6.7 \times 10^{-10} = \dfrac{[OH^-]^2}{0.137}$; $[OH^-] = 9.6 \times 10^{-6}$; % ionization $\ll$ 5% ; assumption valid

pOH = 5.02 ; pH = 8.98

51. (a) mass of solution = 30.0 g ; mass HClO = (30.0 g)(0.10) = 3.00 g

mol HClO = (3.00 g)(1 mol/52.46 g) = 0.0572 ; $[HClO]_o = 0.0572 \text{ mol}/0.0300 \text{ L} = 1.91\ M$

$K_a = \dfrac{[H^+][ClO^-]}{[HClO] - [H^+]}$; $[H^+] = [ClO^-]$; assume $[H^+] \ll [HClO]$

$2.8 \times 10^{-8} = \dfrac{[H^+]^2}{1.91}$; $[H^+] = 2.3 \times 10^{-4}$; % ionization $\ll$ 5% ; assumption valid ; pH = 3.64

(b) At half-equivalence: $[H^+] = K_a = 2.8 \times 10^{-8}$; pH = 7.55

(c) $(\text{mol } ClO^-)_{eq} = (\text{mol } HClO)_o = 0.0572$; mol KOH = mol OH^- = mol HClO = 0.0572

$V_{KOH} = (0.0572 \text{ mol})(1\text{L}/0.419 \text{ mol}) = 0.137$ L; $V_{tot} = (0.137 + 0.030)$ L = 0.167 L

$[ClO^-] = 0.0572 \text{ mol}/0.167 \text{ L} = 0.343\ M$

$K_b = \dfrac{[HClO][OH^-]}{[ClO^-] - [OH^-]}$; $[HClO] = [OH^-]$; assume $[OH^-] \ll [ClO^-]$

$3.6 \times 10^{-7} = \dfrac{[OH^-]^2}{0.343}$; $[OH^-] = 3.51 \times 10^{-4}$; % ionization = 0.102 ; assumption valid

pOH = 3.45 ; pH = 10.54

53. pH = 4.50 ; $[H^+] = 3.2 \times 10^{-5}\ M$

mol Lac^- = mol NaLac = (250.0 g)(1 mol/112.1 g) = 2.230 mol

$[H^+] = K_a \dfrac{\text{mol HLac}}{\text{mol Lac}^-}$; $\text{mol HLac} = \dfrac{(3.2 \times 10^{-5})(2.230)}{1.4 \times 10^{-4}} = 0.51$

mass HLac = (0.51 mol)(90.1 g/mol) = 46 g ; $\text{mass HLac solution} = \dfrac{46 \text{ g}}{0.73} = 63 \text{ g}$

Volume HLac solution = (63 g)(1 mL/1.20 g) = 52 mL

55. pH = 2.95 ; $[H^+] = 1.1 \times 10^{-3}\ M$

$K_a = \dfrac{[H^+][Ac^-]}{[HAc] - [H^+]}$; $[H^+] = [Ac^-]$; assume $[H^+] \ll [HAc]$

$1.8 \times 10^{-5} = \dfrac{(1.1 \times 10^{-3})^2}{[HAc]}$; [HAc] = 0.067 M ; % ionization $\ll$ 5% ; assumption valid

Assume 1000.0 mL of "vinegar" = 1050.0 g of "vinegar" ; mass HAc = (0.067 mol)(60.0 g/mol) = 4.02 g

% HAc in "vinegar" = (4.02/1050) × 100% = 0.38%. Solution *cannot* be called vinegar.

57. (a) mol OH^- = mol KOH = (0.03262 L)(0.730 mol/L) = 0.0238 mol

mol HUric = mol OH^- = 0.0238 ; MM HUric = 4.00 g/0.0238 mol = 168 g/mol

(b) pH = 4.12 ; $[H^+] = 7.6 \times 10^{-5}\ M$; mol OH^- = mol KOH = (0.01200 L)(0.730 mol/L) = 0.00876

mol $Uric^-$ formed = mol OH^- = 0.00876 ; mol HUric left = 0.0238 − 0.00876 = 0.0150

$[H^+] = K_a \dfrac{\text{mol HUric}}{\text{mol Uric}^-}$; $7.6 \times 10^{-5} = K_a \dfrac{0.0150}{0.00876}$; $K_a = 4.4 \times 10^{-5}$

59. $\Pi = MRT$; $M = \dfrac{0.878 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.0359$ mol/L

pH = 6.76 ; $[H^+] = 1.7 \times 10^{-7}$

$K_a = \dfrac{[H^+][X^-]}{[HX] - [H^+]}$; $[H^+] = [X^-]$; assume $1.7 \times 10^{-7} \ll 0.0359$

$K_a = \dfrac{[H^+]^2}{[HX]} = \dfrac{(1.7 \times 10^{-7})^2}{0.0359} = 8.4 \times 10^{-13}$; $K_b = \dfrac{1.0 \times 10^{-14}}{8.4 \times 10^{-13}} = 0.012$

61. (a) 8 □○, 2 ○ (b) 5 □○, 5 ○ (half-neutralization)

(c) 10 ○ (d) 10 ○ , 2 △

63. (a) weak (b) at 25 mL, pH ≈ 3.3 = pK_a; $K_a \approx 5 \times 10^{-4}$ (c) ≈ 8.5

65. (a) GT (b) GT (c) GT (d) EQ

67. (a) False; $[CHO_2^-]$ = 0.1 M only in 0.1 M $NaCHO_2$

(b) True

(c) False; combining a conjugate acid-base pair

(d) False; K_b for $HCO_3^- = 2.3 \times 10^{-8}$; K_b for $CO_3^{2-} = 2.1 \times 10^{-4}$

69. (a) acid (b) C (c) $\approx 10^{-8}$ (d) 0.1 (e) ≈ 5

70. at 1/3 neutralization, one mole of base is formed for every three moles of acid to be neutralized.

Thus two moles of acid are left.

$[H^+] = 6.7 \times 10^{-4} \times \frac{2}{1} = 1.3 \times 10^{-3}$; pH = 2.9

71. $6.3 \times 10^{-5} = 1.8 \times 10^{-5} \times \frac{\text{mol HAc}}{\text{mol Ac}^-}$; $\frac{\text{mol HAc}}{\text{mol Ac}^-} = 3.5$

molOH^- = (0.100 L)(1.25 mol/L) = 0.125 = mol Ac^-; mol HAc for the buffer = (3.5)(0.125) = 0.44

mol HAc needed = 0.125 (to form Ac^-) + 0.44 (HAc needed in buffer) = 0.56

V = [34 g HAc(0.98)](1 mL/1.0542 g) = 33 mL

72. pH of original solution = 2.56; $[H^+] = 2.8 \times 10^{-3}$;

$K_a = 5.5 \times 10^{-5}$ At half-neutralization, pH = 4.25

$5.5 \times 10^{-5} = \frac{(2.8 \times 10^{-3})^2}{[HA]}$; [HA] = 0.14 M

mol HA = (0.14 mol/L)(0.250 L) = 0.034; MM HA = (4.0 g)(0.034 mol) = 1.2×10^2 g/mol

73. pH is 6.50; $[H^+] = 3.16 \times 10^{-7}$

$[H^+] = K_a \times \frac{\text{mol } NH_4^+}{\text{mol } NH_3}$; $3.16 \times 10^{-7} = 5.6 \times 10^{-10} \times \frac{\text{mol } NH_4^+}{\text{mol } NH_3}$; $\frac{\text{mol } NH_4^+}{\text{mol } NH_3} = 565$

One would need 500 times as much NH_4^+ as NH_3.

74. (a) $\frac{[H^+]^2}{1.000} = 6.0 \times 10^{-4}$; $[H^+] = 2.4 \times 10^{-2}\ M$; pH = 1.61

(b) pH = pK_a = 3.22

(c) mol NO_2^- = (1.000 mol/L)(0.0500 L) = 0.0500 ; $V_{NaOH} = \frac{0.0500 \text{ mol}}{0.850 \text{ mol/L}} = 0.0588$ L

V_{tot} = 0.0500 L + 0.0588 L = 0.109 L ; $[NO_2^-]$ = 0.0500 mol/0.109 L = 0.459 M

$\frac{[OH^-]^2}{0.459} = 1.7 \times 10^{-11}$; $[OH^-] = 2.8 \times 10^{-6}\ M$; pOH = 5.55; pH = 8.45

(d) mol HNO_2 left = $(1.0 \times 10^{-4}$ L)(0.850 mol/L) $= 8.50 \times 10^{-5}$

$[H^+] = 6.0 \times 10^{-4} \times \frac{8.50 \times 10^{-5}}{0.0500} = 1.0 \times 10^{-6}\ M$; pH = 6.00

(e) mol OH^- = $(1.0 \times 10^{-4}$ L)(0.850 mol/L) $= 8.50 \times 10^{-5}$

$$[OH^-] = \frac{8.50 \times 10^{-5}\text{ mol}}{0.109\text{ L}} = 7.8 \times 10^{-4}\,M\text{ ;}\quad \text{pOH} = 3.11\text{ ; pH} = 10.89$$

(f) Similar to Figure 14.6 but pH is somewhat lower because HNO_2 is a stronger acid than $HC_2H_3O_2$.

75. $1.0 \times 10^{-5} = 1.8 \times 10^{-5} \times \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]}$; $\quad \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]} = 0.56$

fraction neutralized = $\frac{1.00}{1.56} = 0.64$; 32 mL NaOH

76. (a) $[H^+] = 0.1500\,M$ pH = 0.82

(b) $0.011 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.1500 + x)(x)}{0.1500 - x}$

Solving for x using the quadratic equation, $x \approx 0.01$; $[H^+] = 0.16\,M$; pH = 0.80

77. $[H^+] = K_a \times \frac{[HB]}{[B^-]} = K_a \times \frac{7.00}{14.0}$; $\quad K_a = 2\,[H^+] = 2(1.1 \times 10^{-9})$; $\quad K_b = \frac{1.0 \times 10^{-14}}{2.2 \times 10^{-9}} = 4.5 \times 10^{-6}$

78. mol NH_3 = (0.150 mol/L)(1.000 L) = 0.150 ; mol NH_4^+ = mol NH_4Cl = (10.0 g)(1 mol/53.49 g) = 0.187

$[H^+] = 5.6 \times 10^{-10} \times \frac{0.187}{0.150} = 6.98 \times 10^{-10}$; pH = 9.16

new pH = 9.16 + 1.00 = 10.16 ; $[H^+] = 6.98 \times 10^{-11}$

Let x = mol OH^- that react with NH_3; $\quad 6.98 \times 10^{-11} = 5.6 \times 10^{-10} \times \frac{0.187 - x}{0.150 + x}$; $\quad x = 0.15$ mol OH^-

mass NaOH = (0.15 mol)(40.0 g/mol) = 6.0 g

79. $\log_{10}[H^+] = \log_{10} K_a + \log_{10}\frac{[HB]}{[B^-]}$

Multiply by (– 1): $\text{pH} = \text{p}K_a + \log_{10}\frac{[B^-]}{[HB]}$